Properties of Monomeric and Polymeric Alkyl Acrylates and Methacrylates

C. E. REHBERG AND C. H. FISHER

Eastern Regional Research Laboratory, Philadelphia 18, Pa.

The preparation and certain physical properties of various alkyl methacrylates, particularly the n-alkyl esters, are described. The curve obtained by plotting brittle points of the polymeric n-alkyl methacrylates against carbon atoms in the alkyl group is similar in shape to the corresponding curve of the n-alkyl acrylates. The brittle points of the n-alkyl polymethacrylates decrease with increasing molecular weight to the dodecyl ester (brittle point, $-34°$ C.) and then increase. Cetyl polymethacrylate, the highest alkyl ester studied, had a brittle point of 15° C. The brittle points of the first eight n-alkyl polyacrylates and twelve n-alkyl polymethacrylates are straight-line functions of the logarithm of the carbon atoms in the alkyl groups. Williams plastometer values of the polymeric n-alkyl acrylates, used as a measure of hardness, decreased with increasing molecular weight to approximately the nonyl ester. The plastometer values were proportional to the brittle points for the methyl to nonyl acrylates. Williams plastometer values obtained with the polymers of n-butyl, n-amyl, n-octyl, and n-decyl polymethacrylates decreased with increase in the length of the alkyl groups. The plastometer values of these polymeric methacrylates were found to be proportional to the brittle points.

IN PREVIOUS papers (*11, 12*) the preparation of various alkyl acrylates by a convenient method was described, and certain properties of the monomeric and polymeric acrylic esters were reported. This paper contains additional data obtained in a more recent study of acrylic and methacrylic esters. Not all the n-alkyl esters were prepared, but from relationships observed between physical properties and molecular weights the properties of the missing members can be estimated. It is believed that the information reported herein is of value because of the growing importance of acrylates and methacrylates and the fact that earlier data on the subject, usually reported in patent literature, are either inadequate or unreliable.

MONOMERIC ESTERS

Alcoholysis, a method previously employed (*2, 6, 7, 11, 12, 16*) in the preparation of both acrylic and methacrylic esters, was used in most instances in this work to make the higher alkyl crylates and methacrylates. n-Tetradecyl methacrylate was made from methacrylic anhydride and the alcohol.

The boiling points of n-alkyl acrylates and methacrylates at different pressures are given in Figures 1 and 2. The boiling points at 10 and 760 mm. may be calculated from the total number of carbon atoms, x, by Equations 1 to 4 ($T = $ ° K.).

This method for relating boiling points at 760 mm. to number of carbon atoms has been used previously (*1, 4, 8*). This relationship and those represented by other equations of this paper are usually unsatisfactory for the first two or three members of a homologous series.

The boiling points (° C.) at 760 mm. of the n-alkyl acrylates and methacrylates, B_E, can be estimated also from the boiling points of the corresponding alcohols, B_A, by Equations 5 and 6 (Figure 3):

$$n\text{-Alkyl acrylates at 10 mm.} \quad T^2\, 10^{-4} = 1.16\, x + 1.30 \quad (1)$$
$$\text{at 760 mm.} \quad T^2\, 10^{-4} = 1.87\, x + 4.40 \quad (2)$$
$$n\text{-Alkyl methacrylates at 10 mm.} \quad T^2\, 10^{-4} = 1.11\, x + 1.50 \quad (3)$$
$$\text{at 760 mm.} \quad T^2\, 10^{-4} = 1.84\, x + 4.20 \quad (4)$$

$$\text{Acrylates } B_E = 1.07\, B_A + 18 \quad (5)$$
$$\text{Methacrylates } B_E = 1.02\, B_A + 41 \quad (6)$$

The boiling points at 760 mm. of the n-alkanols may be calculated ($T = $ ° K., $x = $ carbon atoms):

$$T^2\, 10^{-4} = 1.68\, x + 8.50$$

With the exception of the first two members of the homologous series, straight lines were obtained by plotting refractive indexes of n-alkyl butyrates (*3, 9, 13*) against those of the corresponding alkyl acrylates and methacrylates (Figure 4 and Table I).
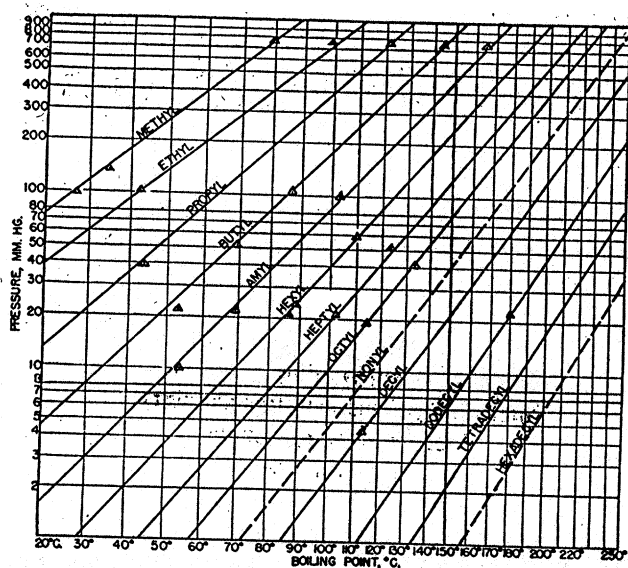
Figure 1. Boiling Points of n-Alkyl Acrylates

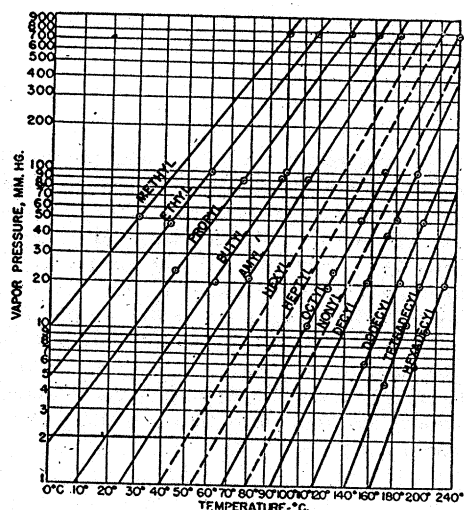Location of lines for nonyl and hexadecyl esters estimated by use of equation

Refractive indexes, n_D^{20}, of the n-alkyl acrylates and methacrylates can be calculated by Equations 7 and 8 (M = molecular weight; x = total carbon atoms):

$$M/n = 9.519\,x + 23.70 \tag{7}$$

$$n = 1.4735 - \frac{1}{1.9292\,x + 4.8033} \tag{8}$$

Densities, d_4^{20}, of the n-alkyl acrylates and methacrylates are related to molecular weight as shown in Equations 9 to 12 (x = total carbon atoms):

$$\text{Acrylates } M/d = 16.60\,x + 26.30 \tag{9}$$

$$d = 0.8449 + 1/(2.138\,x + 3.39) \tag{10}$$

$$\text{Methacrylates } M/d = 16.50\,x + 27.20 \tag{11}$$

$$d = 0.8501 + 1/(2.404\,x + 3.96) \tag{12}$$

The n-alkyl acrylates and methacrylates of equal molecular weight (excluding the first two or three members) have virtually identical refractive indexes (Table I, Equations 7, 8, and Figure 5). A linear relationship exists between the densities observed for the n-alkyl acrylates and methacrylates (Figure 5), but the methacrylates had higher densities than the isomeric acrylates.

POLYMERIC ESTERS

The alkyl methacrylates were emulsion polymerized by the method employed previously (11, 12) to convert acrylic esters into polymers of relatively high molecular weight. The poly-
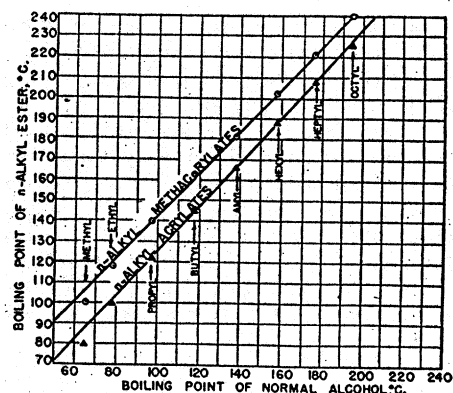

Figure 2. Boiling Points of n-Alkyl Methacrylates

Location of lines for hexyl, heptyl, and nonyl esters estimated by use of equation

Figure 3. Relation between Boiling Points of Normal Alcohols and Corresponding Alkyl Acrylates and Methacrylates

TABLE I. ALKYL METHACRYLATES

Methacrylate	Yield, % of Theoretical	n_D^{20}	d_4^{20}	Mol. Refraction Calcd.	Mol. Refraction Found	Saponification Equivalent Calcd.	Saponification Equivalent Found	Brittle Point of Polymer, °C.
Methyl	a	1.4142	0.9440	26.47	26.54	100.1	101.6	
Ethyl	a	1.4147	0.9135	31.09	31.24	114.1	115.6	90
n-Propyl	92b	1.4190	0.9022	35.71	35.88	128.2	129.0	50
n-Butyl	a	1.4240	0.8936	40.33	40.61	142.2	144.2	36
Isobutyl	a	1.4200	0.8865	40.33	40.60	142.2	143.9	16
n-Amyl	82b	1.4284	0.8890 c	44.95	45.25	156.2	157.2	54
			0.8910		45.15			-5
n-Octyl	a	1.4374	0.8804	58.81	59.05	198.3	200.4	-16
2-Ethylhexyl	98b	1.4390	0.8847	58.81	58.96	198.3	200.4	-10
n-Decyl	74b	1.4418	0.8767	68.05	68.28	226.4	227.3	-28
n-Dodecyl	a	1.4452	0.8735	77.28	77.52	254.4	253.8	-34
n-Tetradecyl	68d	1.4480 d	0.8710 c	86.51	86.81	282.5	281.4	-5
		1.4495	0.8740		86.76			
n-Hexadecyl	a	1.4515	0.8695	95.75	96.24	310.5	315.0	15

a Samples obtained by redistillation of products supplied by the Rohm & Haas Company.
b Prepared by the alcoholysis of methyl methacrylate.
c Smoothed value from curves prepared by plotting n_D^{20} or d_4^{20} against carbon atoms.
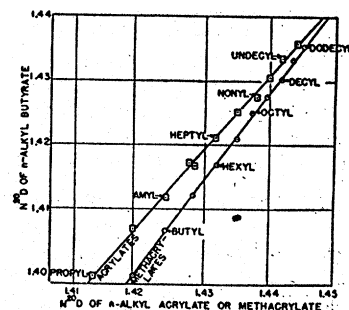d Prepared from methacrylic anhydride and the alcohol.

Figure 4. Relation between Refractive Indexes of n-Alkyl n-Butyrates and Corresponding n-Alkyl Acrylates and Methacrylates
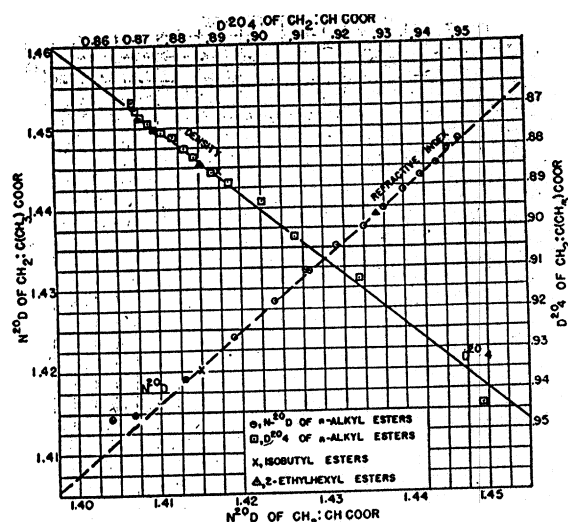
Figure 5. Relation between Physical Properties of Alkyl Acrylates and Corresponding Alkyl Methacrylates

showing the relationship between plasticity data and number of carbons in the alkyl group are somewhat similar to the brittle point curve of Figure 6. Apparently a linear relationship exists between Williams plasticity data and brittle points for the first several n-alkyl polyacrylates and polymethacrylates (Figure 11).

Figure 6

EXPERIMENTAL

Methyl, ethyl, n-butyl, isobutyl, n-octyl, n-dodecyl, and n-hexadecyl methacrylates were kindly furnished by the Rohm and Haas Co. These were distilled through fractionating columns having the equivalent of 20 to 40 theoretical plates. n-Propyl, n-amyl, 2-ethylhexyl, and n-decyl methacrylates were prepared by the procedure previously described (12) for the

mers, which were prepared under similar conditions, were examined to determine the relationships between the number of carbon atoms in the monomeric ester and brittle point and hardness of the polymer. (One of the reviewers has pointed out that the higher n-alkyl polyacrylates and polymethacrylates form relatively hard, brittle, opaque, and apparently crystalline waxes having fairly sharp melting points and that, in Figure 6, the left-hand portions of the curves represent brittle points whereas the right-hand portions represent melting points of these crystalline waxes.)

The curve obtained by plotting the brittle points of the polymeric n-alkyl methacrylates against the number of carbon atoms in the n-alkyl group is roughly similar in shape to the corresponding curve for the polyacrylic esters (Figure 6). However, the lowest point (−34° C.) of the curve is reached with the dodecyl ester, whereas octyl polyacrylate has the lowest brittle point (−65° C.) of the acrylic polymers. The two curves cross at the decyl esters. Unless the curves cross again at some ester higher than n-octadecyl, many polymeric n-alkyl acrylates— that is, all except the first nine or ten members—have higher brittle points than the corresponding methacrylates.

The brittle points of the first eight acrylates and twelve methacrylates are straight-line functions of the logarithm of the carbon atoms in the alkyl groups (Figure 7).

Comparison of the brittle points of isobutyl and 2-ethylhexyl polymethacrylates with those of the isomeric n-butyl and n-octyl esters indicates that branching of the alkyl group raises the brittle point in the methacrylate series. This effect of branching on the brittle point has been observed previously for both acrylates (10, 11) and methacrylates (5, 14).

Williams (17) plasticity data were determined and used as measure of the hardness of the polymers (Figures 8, 9, 10, and Tables II, III). As might be expected, the curves
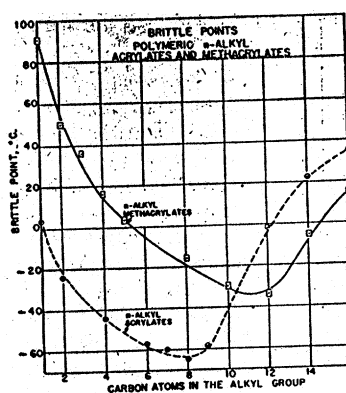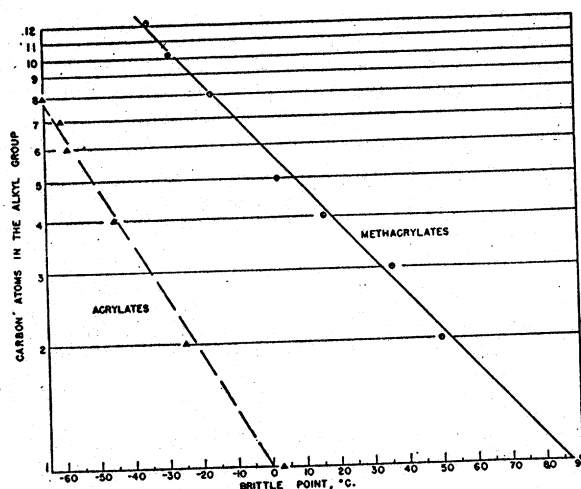
Figure 7. Brittle Points of Polymeric n-Alkyl Acrylates and Methacrylates

TABLE II. WILLIAMS PARALLEL PLATE PLASTOMETER READINGS WITH POLYACRYLIC ESTERS

(2-gram spheres at 26° C.)

Polyacrylic Ester	Centimeters, at										
	15 sec.	30 sec.	1 min.	2 min.	3 min.	5 min.	10 min.	15 min.	25 min.	35 min.	45 min.
Methyl	0.213	0.209	0.2062	0.2032	0.2015	0.1995	0.1963	0.1945	0.1925	0.1913	0.1905
Ethyl	0.140	0.138	0.1365	0.134	0.1325	0.131	0.1285	0.1265	0.1242	0.123	0.1228
n-Propyl	0.154	0.148	0.1445	0.1405	0.1383	0.1355	0.132	0.130	0.1278	0.126	0.1247
n-Butyl	0.148	0.1405	0.1335	0.126	0.122	0.117	0.1105	0.1065	0.1025	0.0993	0.0972
n-Octyl	0.087	0.081	0.0755	0.0705	0.068	0.065	0.0615	0.0592	0.0565	0.0551	0.0538
n-Nonyl	0.078	0.073	0.0695	0.0655	0.063	0.0608	0.0575	....	0.053	0.051	0.051
n-Tetradecyl	0.076	0.073	0.071	0.0695	0.067	0.0655	0.063	0.0613	0.0595	0.0583	0.0575

TABLE III. WILLIAMS PARALLEL PLATE PLASTOMETER READINGS WITH POLYMETHACRYLIC ESTERS

(2-gram spheres at 26° C.)

| Polymeth-acrylic Ester	Centimeters, at											
	10 sec.	30 sec.	1 min.	2 min.	3 min.	5 min.	10 min.	15 min.	20 min.	30 min.	45 min.	60 min.	90 min.
n-Butyl	0.601	0.592	0.581	0.565	0.555	0.540	0.516	0.501	0.490	0.474	0.457	0.445	0.430
n-Amyl	0.355	0.320	0.303	0.290	0.283	0.275	0.264	0.258	0.254	0.248	0.241	0.236	0.229
n-Octyl	0.180	0.170	0.163	0.155	0.150	0.145	0.136	0.132	0.127	0.122	0.117	0.113	0.108
n-Decyl	0.111	0.097	0.089	0.081	0.075	0.070	0.063	0.060	0.057	0.054	0.051	0.049	0.046
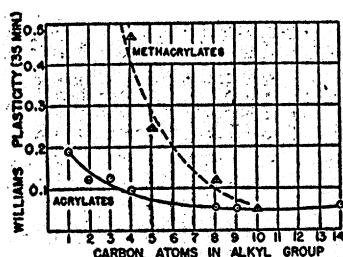
Figure 8. Relation between Williams Plasticity and Carbon Atoms in Alkyl Group of Polymeric n-Alkyl Acrylates and Methacrylates

alcoholysis of methyl methacrylate.

Fractionating columns having high capacity and a large number of theoretical plates greatly accelerate the alcoholysis when primary alcohols are used. For fastest reaction it is essential that the by-product alcohol be removed as fast as form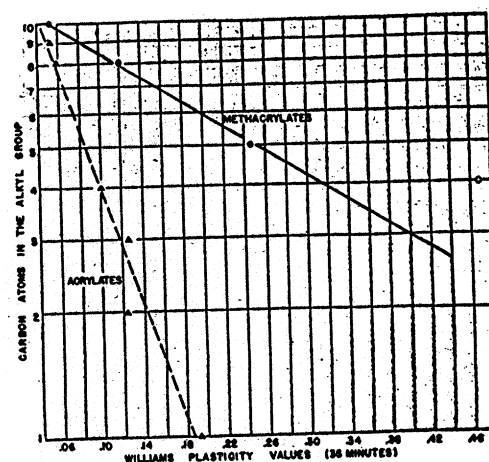ed; this required that the column have both a suitable capacity for the size of the reaction mixture and high enough efficiency to separate sharply the azeotrope of the by-product alcohol and the lower ester from the lower ester. This separation is relatively easy when using methyl methacrylate or ethyl acrylate but more difficult when using methyl acrylate.

Most of the authors' earlier work (11, 12) was done with columns having 5 to 10 theoretical plates and relatively low capacity. Later work with columns having 20 to 50 theoretical plates and higher capacity has revealed previously undetected differences in the rate of reaction of various alcohols. For instance, in the earlier work 2-ethylhexanol and 2-octanol appeared to react at about the same rate. In experiments with the more efficient columns, the former reacted three or four times as fast as the latter. Most of the primary alcohols require 4 to 8 hours for the alcoholysis to reach 90 to 95% completion.

n-TETRADECYL METHACRYLATE. One mole of myristyl alcohol, 0.5 cc. of sulfuric acid, and 1 gram of copper powder were put in a flask fitted with a stirrer and dropping funnel. While the con-

Figure 9. Williams Plasticity of Polymeric n-Alkyl Acrylates and Methacrylates as a Function of Carbon Atoms in Alkyl Groups

tents of the flask were kept at about 80° C., 1.1 moles of methacrylic anhydride were slowly added. When addition was complete, the mixture was heated at 100° C. for 3 hours and then left overnight. Two grams of sodium acetate were added to neutralize the sulfuric acid, and the mixture was distilled through a short column. The product boiled at 140° to 145° C. (0.2 mm.), and the yield was 68%. A large polymeric residue remained; this indicated that the copper powder was an inadequate inhibitor. The product was redistilled through an efficient column without formation of polymer; diamylhydroquinone was used as an inhibitor.

ISOBUTYL AND 2-ETHYLHEXYL METHACRYLATES. These boiled at 52° C. (12 mm.) and 88° C. (3.5 mm.), respectively; the boiling points of the other methacrylates are shown in Figure 2. 2-Ethylhexyl methacrylate and several acrylic esters exploded with violence during attempts to determine carbon and hydrogen by dry combustion (observation by C. O. Willits and associates of this laboratory).

n-ALKYL ACRYLATES. The following constants for the n-alkyl acrylates are now preferred to those previously published: amyl, d_4^{20}, 0.8920; hexyl, n_D^{20}, 1.4280; heptyl, n_D^{20}, 1.4317; octyl, n_D^{20}, 1.4350; nonyl, n_D^{20}, 1.4375.

POLYMERIZATION. The methacrylates were polymerized in emulsion; Triton 720 (15) was used as emulsifier and ammonium persulfate or benzoyl peroxide as catalyst. Benzoyl peroxide was used because the persulfate was ineffective with dodecyl and higher esters. Most of the polymers of the higher acrylates and methacrylates were incompletely soluble in the organic solvents tested. Therefore, intrinsic viscosities were not determined. Brittle points were determined, as previously described for the polyacrylates (11), by flexing strips of the polymer (roughly 0.08 inch thick) and noting the temperature at which the samples broke because of brittleness. Samples were immersed for approximately 2 minutes before flexing.
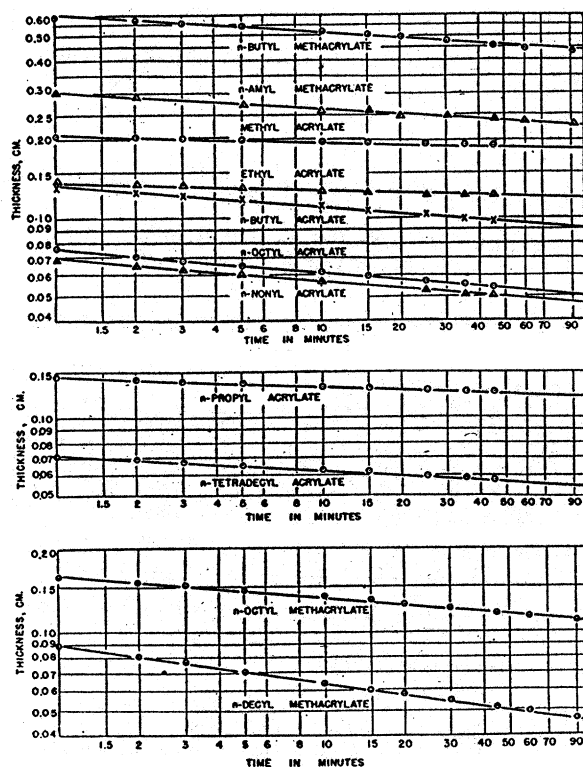

Figure 10. Williams Plastometer Readings Obtained at Room Temperature with Polymeric Acrylates and Methacrylates
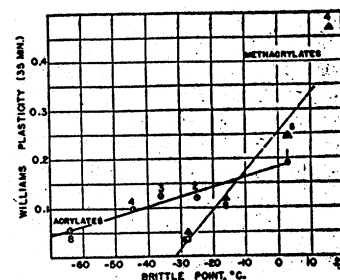

Figure 11. Relation between Williams Plasticity and Brittle Points of Polymeric n-Alkyl Acrylates and Methacrylates

Numbers indicate carbon atoms in alkyl groups

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